

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in the Curing of Epoxy Resins

We, EXPANDITE LIMITED, a British Company, of Chase Road, London, N.W.10, and YARSLEY RESEARCH LABORATORIES LIMITED, a British Company, of "Oaklands", Clayton Road, Chessington, Surrey, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to epoxy resins which are polyglycidyl ethers of polyhydric phenols or polyhydric alcohols.

Epoxy resins are commonly cured, or caused to harden, by the addition of a curing or hardening agent. Many of the curing agents hitherto used have begun to act at once, or after only a short time, even at room temperature. The resin and the curing agent have therefore had to be stored separately and only mixed immediately before use. This was inconvenient, and also led to wastage if more mixture was prepared than could be used at once. Moreover many of the aliphatic and aromatic amines commonly employed for curing epoxy resins, e.g. diethylene triamine, triethylene tetramine and metaphenylene diamine, suffer from the disadvantage that they exhibit skin-sensitising properties and can produce dermatitic conditions in certain sensitive individuals.

This invention is based on the discovery that mixtures of epoxy resins having a 1,2-epoxy equivalency greater than one with amine salts of hydrofluoboric acid can be stored for prolonged periods at room temperature without polymerisation occurring and can then be caused to polymerise rapidly by heating to moderate temperatures, forming hard tough solids. The term "1,2-epoxy equivalency" refers to the number of 1,2-epoxy groups contained in the average molecule of epoxy resin. The 1,2-epoxy equivalency is obtained by dividing the average molecular weight of the resin by the epoxide equivalent weight (the weight of the resin in grams which contains 1 gram-molecule of epoxy oxygen). The invention includes broadly as novel composition of matter which set solid on heating such an epoxy resin and curing agents with or without other ingredients.

When prepared at room temperature the compositions in general have a pot life of at least 24 hours throughout which the composition remains in a non-hardened, or non-cured, workable state. The necessity of keeping the hardener, or curing agent, separate from the epoxy resin until immediately prior to use is thus avoided and these compositions can be stored at an ambient temperature as a one-part mix.

One feature of the invention is thus the making of the compositions at room temperature, storing them for a period of 24 hours or more without substantial polymerisation and then causing them to polymerise by heating. Polymerisation is rapid at moderately elevated temperatures and in general can be made to go substantially to completion within a few seconds to a few minutes on heating to 100° C. The polymerisation reaction is highly exothermic and this assists in obtaining a well cross-linked and thoroughly cured product.

The actual curing time (by which is meant the time required for the resin to polymerise to a hard, thermoset, insoluble final product) will depend on the nature of the resin, the mode of incorporation of the amine salt into the resin, and the temperature. Solid amine salt may, for instance, be finely ground and milled in a powder form into the epoxy resin or taken up in a suitable solvent and the solution so formed used as the curing agent. If the amine salt is used in the form of a solution the curing time may also depend on the nature of the solvent used and the concentration of the amine salt in the solvent. In general, however, we find that satisfactory results may be obtained by the use of at least 0.5% of the amine salt by weight of the epoxy resin.

The amine used to form the salt may be a primary, secondary, or tertiary aliphatic or aromatic amine, heterocyclic amine, or alicyclic amine, with or without nuclear or side-chain substituents. However the aromatic amines are definitely preferred since the salts of some of the other amines, for example of some of the aliphatic amines only act as curing agents at rather high temperatures, say 200° C. Preferred aromatic amine salts are those formed from metaphenylene diamine, paraphenylene diamine, aniline, N-mono- and N-dialkyl-anilines, the salt being formed by the reaction of the acid with the primary, secondary or tertiary amino groups, or all three types of amine groups. Salts of polyamines in which all the amino groups are combined with acid, e.g. metaphenylene diamine difluoroborate, are not so satisfactory as those which still have free amine groups, and we prefer not to use salts of amines having acidic constituents, for example the fluoroborates of ortho- and para-aminobenzoic acid.

The following examples illustrate the preparation of amine salts suitable for use as curing agents for the purpose of this invention. The parts quoted are by weight.

EXAMPLE I.

Metaphenylene diamine monohydro-fluoroborate (hereinafter called AS1) was prepared by the dropwise addition of a solution of 108 gms. of metaphenylene diamine dissolved in acetone to 220 gms. of a 40% aqueous solution of hydrofluoboric acid. The reaction was carried out at room temperature and an orange red crystalline product was obtained from the reaction mixture by vacuum evaporation of the solvent, and was found to be stable at room temperature, non-deliquescent and non-hygroscopic.

EXAMPLE II.

Aniline hydrofluoroborate (hereinafter called AS2) was prepared by the addition of 93 gms. of aniline to 220 gms. of a 40% aqueous solution of hydrofluoboric acid. The reaction was carried out at room temperature and a pale brown crystalline product obtained from the reaction mixture by evaporation, which was found to be stable at room temperatures, non-deliquescent and non-hygroscopic.

The amine salts AS1 and AS2 are incompatible in the solid phase with liquid epoxy resins. They can, however, be finely powdered and milled into a liquid epoxy resin to give a composition which has a pot life at room temperature of more than 24 hours and which upon heating to moderately elevated temperatures polymerises to give a hard, thermoset, insoluble, infusible product. The amine salts AS1 and AS2 are soluble in a wide range of organic solvents to give solutions which are compatible with liquid epoxy resins at room temperature and a composition consisting of a liquid epoxy resin and a solvent solution of an amine salt can be polymerised at moderately elevated temperatures to give a hard, thermoset, insoluble, infusible product. Where a solvent solution of the curing agent has been employed to facilitate uniformity of distribution of the curing agent in the epoxy resin, it is desirable, in order to prevent foaming and obtain pore-free polymers, to remove the solvent prior to polymerisation. Suitable solvents which may be used for the purpose of obtaining solutions of the amine salts are acetone, ethyl alcohol, and dioxane.

The invention is applicable to any epoxy resin, by which we mean a polyglycidyl ether of a polyhydric phenol or a polyhydric alcohol, which has a 1,2-epoxy equivalency greater than one, and where the resin consists of a known, individual compound the epoxy equivalency will be an integer of two or more. For example the epoxy equivalency of diglycidyl ether or of the diglycidyl ether of ethylene glycol is two, while that of the triglycidyl ether of glycerol is three.

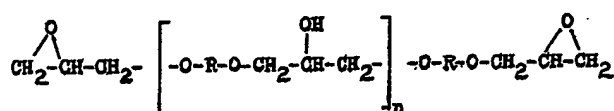
However, the epoxy resins may be a mixture of chemical compounds, which, although they are of similar identity and chemical constitution, have different molecular weights. The measured molecular weight of the mixture upon which the epoxide equivalent weight is dependent will then necessarily be an average, and consequently the epoxy equivalency of the epoxy resin while still having a value which is greater

than one, will not necessarily be an integer of two or more. For example, an epoxy resin particularly suitable for use in the invention is that made by reacting bis-(4-hydroxyphenyl)2,2-propane with epichlorhydrin in alkaline solution. The products of this reaction having an epoxy equivalency greater than one are mixtures of glycidyl ethers with a measured average molecular weight of not less than 340, and may be resinous liquids or solids.

Epoxy resins having a 1,2-epoxy equivalency of more than one may be made from any of the various polyhydric phenols, for example the mono-nuclear phenols resorcinol, catechol, hydroquinone, and phloroglucinol and the poly-nuclear phenol bis-(4-hydroxyphenyl)-2,2-propane (bisphenol A).

Typical epoxy resins which may be cured according to the invention are the glycidyl ethers of the dihydric phenols. These substances may be prepared by heating the dihydric phenol at 50° C. to 150° C. with epichlorhydrin, using more than one mole of epichlorhydrin per mole of dihydric phenol, in the presence of a base, e.g. sodium, potassium, calcium or barium hydroxide, in amount of about 10% to 30% stoichiometric excess of the epichlorhydrin.

The resulting resinous glycidyl ether is a complex mixture rather than a single chemical compound. The principal product may be represented by the formula:



where n is 0, or any integer, and R represents the di-valent hydrocarbon radical of the dihydric phenol. The length of the chain (the value of n) can be made to vary by changing the molecular proportions of epichlorhydrin to dihydric phenol in preparing the glycidyl ether. Thus, by decreasing the number of moles of epichlorhydrin per mole of dihydric phenol from about two downwards towards one, the molecular weight and softening point are increased. In general, these glycidyl ethers have an epoxy equivalency between 1 and 2, contain terminal 1,2-epoxy groups and have alternate aliphatic and aromatic groups linked together by ethereal oxygen atoms.

Another class of epoxy resins that are particularly suitable for use in the invention is obtained by reacting epichlorhydrin or dichlorhydrin with polyhydric alcohols and subsequently treating the resulting product with an alkali. Examples of polyhydric alcohols that may be used for this purpose are glycerol, ethylene glycol, hexanetriols, sorbitol, mannitol, pentaerythritol, glycerol α -mono-methyl ether, polyvinyl alcohol, and polyallyl alcohol.

The following table characterises some specific examples of epoxy resins prepared by the reaction of polyhydric phenols with epichlorhydrin that may be polymerised by amine salts or solutions thereof. Resin A was derived from equivalent proportions of hydroquinone and epichlorhydrin, whereas resins B, C and D were obtained by the reaction of bis-phenol A with varying proportions of epichlorhydrin.

TABLE I

Resin	Average epoxide equivalent weight	Average molecular weight	Epoxy equivalency
A	111	222	2.00
B	185/200	350/400	1.95
C	175/210	350/400	1.95
D	450/525	900/1000	1.95

The following examples illustrate the use of the amine salts AS1 and AS2 as curing agents for the resins B and C, and also illustrate the variations in curing time

that may be obtained by using the solid amine salts, or a solution of the amine salts in different solvents.

EXAMPLE III.

The following example shows how the curing time can be varied by using different combinations of the solid amine salt AS1 and epoxy resin.

(a) 0.01 gms. of AS1 in a finely powdered state was thoroughly mixed into 1 gm. of resin B. The composition was stable for at least 24 hours at room temperature, but on being heated to 100° C. a hard, thermoset, insoluble product was obtained in 2½ minutes.

(b) 0.15 gms. of the above salt was thoroughly mixed into 1 gm. of resin C. The composition was stable for at least 24 hours at room temperature but on being heated to 100° C. gave a hard, thermoset, insoluble, infusible product in 1½ minutes.

EXAMPLE IV.

The following example shows how the curing time can be varied by using different volumes of the same concentration of amine salt AS1 and AS2 in solvents.

(a) Using 0.2 ml. of a 66% solution in acetone of amine salt AS1 a curing time of 1 minute at 100° C. was obtained with 1 gm. of resin B.

(b) 0.25 ml. of the above solution gave a curing time of 2½ minutes at 100° C. with 1 gm. of resin C.

(c) 0.05 ml. of a 20% solution of amine salt AS2 in ethanol gave a curing time of 1 minute 24 seconds at 100° with 1 gm. of resin B.

(d) 0.025 ml. of the same solution giving a curing time of 1 minute 46 seconds at 100° C. with 1 gm. of resin C.

All the compositions were stable for at least 24 hours at room temperature.

The product after curing in each case was a hard, thermoset, insoluble mass.

The storage life of the above compositions when the salt is an aromatic amine salt may be still further prolonged while still retaining the property of curing rapidly at moderately elevated temperatures by the incorporation of a proportion of a free primary or secondary aromatic amine or primary or secondary aromatic amide not exceeding 5% by weight of the resin.

It is particularly surprising that primary amines should have this effect, since in quantities sufficient to react with substantially all the epoxy groups present these are commonly used as curing agents for epoxy resins. In compositions according to the invention primary aromatic amines are still effective in cross-linking the epoxy resins, and thus participate in the curing, and we therefore prefer to use these as the room-temperature retardants.

Some retarding effect is obtained even with very small additions of primary or secondary aromatic amines, e.g. 0.1% by weight of resin. We find however that if the proportion of primary aromatic amine in the composition is too high it also promotes the curing at room temperature by acting as a cross-linking agent instead of a retardant, and care should therefore be taken not to add so much that the retarding effect is lost. With secondary amines, on the other hand, it is found that the addition of an excessive amount inhibits the curing of the resin even at high temperatures. The upper limits of concentration at which a primary amine ceases to act as a retardant or a secondary amine slows down the rate of curing to an impractical extent varies with the nature of the amine, and must be determined experimentally for any given combination of epoxy resin, amine salt and amine. The amount of amine used in general will not exceed 5% by weight of the resin and will in any case only be sufficient to react with a small proportion of the epoxy groups present.

The amine fluoborate used in the composition as the principal curing agent is preferably a fluoborate of a primary aromatic amine.

The process of the invention is further illustrated by means of the following examples. The resin used in all cases was Epikote 828, which is the Registered Trade Mark for an epoxy resin derived from epichlorohydrin and bisphenol A having a specific gravity of 1.2 an epoxide value of 0.52, a hydroxyl value of 0.08, and an esterification value of 1.26, these values being expressed in gram equivalents per 100 grams.

EXAMPLE V.

25 gms. aniline fluoborate were dissolved in 75 gms. of acetone and the solution was mixed with 2425 gms. of Epikote 828, giving a mixture containing 1% aniline fluoborate by weight.

Free amine was dissolved in the resin/amine salt mixture at room temperature or with slight warming, liquid amines being dispersed by simply stirring while solid amines were incorporated with the addition of a small amount of acetone to give the percentages quoted in Table II. It was found that the presence of acetone in the composition in the amounts needed to incorporate the amounts of amine and amine salt used did not appreciably affect the setting time, but the amount of solvent used should be as small as possible. The setting time at the elevated temperatures was determined by heating 0.5—0.8 gms. of the mixture in a small tin of 5 mls. capacity on a thermostatically controlled hot-plate, and the setting time was taken as the time required for the resin to polymerise to a hard, tack-free solid when hot. The storage life at room temperature was determined by allowing a larger quantity of the mixture to stand at the ambient temperature and observing its consistency from time to time.

The results are reproduced in Table II.

TABLE II

Amine	Proportion of amine (% by weight of resin)	Setting time at stated temperature					
		160°C.		100°C.		Room temp.	
Nil		50	secs.	150	secs.	16	hours
Aniline	1	60	secs.	6.5	mins		
„	2	60	secs.	20	mins.	14	days
„	4	75	secs.			4	days—B.U.
m-toluidine	1	60	secs.	19.	mins	18	days
„	2	80	secs.	33	mins	30	days
„	4	100	secs.	70	mins	50	days
p-toluidine	1	<1	min.	15	mins.	24	days
„	2	<1	min.	49	mins	35	days
„	4	135	secs.				
p-amino-phenol	$\frac{1}{2}$	75	secs.	15	mins.	38	days
„ „	1	110	secs.	45	mins.	60	days—B.U.
„ „	2	4 $\frac{1}{2}$	mins.	71	mins.	90	days—not set
p-phenylene diamine	$\frac{1}{2}$	90	secs.	20	mins.	35.	days
„	1	4 $\frac{1}{2}$	mins.	2 $\frac{1}{2}$	hrs.		
„	2	15 $\frac{1}{2}$	mins.	3	hrs.	180	days—not set
	4	16 $\frac{1}{2}$	mins.	2 $\frac{1}{2}$	hrs.	100	days—B.U.
o-amino benzoic acid	1	60	secs.	10	mins.		
„	2	70	secs.	30	mins.	150	days—not set
„	4	75	secs.	51	mins.	150	days
β -naphthylamine	$\frac{1}{2}$	60	secs.	6	mins.	6	days
„	1	60	secs.	7 $\frac{1}{2}$	mins.	13	days
„	2	120	secs.	11	mins.	13	days

B.U. = Bodied up

EXAMPLE VI

Similar experiments were carried out using p-toluidine fluoborate in place of aniline fluoborate of Example V. The quantities used were the same as those in that Example. The results are reproduced in Table III.

TABLE III

Amine	Proportion of amine (% by weight or resin)	Setting time at stated temperature					
		160°C.		100°C.		Room temp.	
Nil		1	min.	2	mins.	3	days
Aniline	1	1	min.	12	mins.	24	days
"	2	1	min.	28	mins.	35	days
"	4	80	secs.	45	mins.	35	days
m-toluidine	2	75	secs.	41	mins.	21	days
p-toluidine	1	90	secs.	31	mins.	44	days B.U.
"	2	100	secs.	67	mins.	71	days B.U.
"	4 2 min.	50	secs.	60	mins.	80	days—not set
o-amino benzoic acid	4	70	secs.	67	mins.	29 days 140 days	B.U. B.U.
p-amino phenol	1	60	secs.	65	mins.	150	days
Benzylamine	$\frac{1}{2}$	4	mins.	87	mins.	7	days
	1	16	mins.	75	hours	150	days—not set

EXAMPLE VII

Similar experiments were carried out using the same quantity of β -naphthylamine fluoborate in place of the aniline fluoborate of Example V. The results are summarized in Table IV

TABLE IV

Amine	Proportion of amine (% by weight of resin)	Setting time at stated temp.	
		110°C.	Room temp.
Nil		1	min.
β -naphthylamine	1	2	min.
	2	3	min.
		4	days
		11	days

EXAMPLE VIII

Similar experiments were carried out using the same quantity of aniline fluoborate as in Example V, but using secondary amines. The results are summarised in Table V.

TABLE V

Amine	Proportion of amine (% by weight resin)	Setting time at stated temperature		
		160°C.	100°C.	Room temp.
N-ethylaniline	1	55 secs.		
	1½	80 secs.	65 mins.	
	2	10 mins.	2½ hr. B.U.	112 days not set
	4	90 mins.		
N-ethyl p-toluidine	1	2 mins.		
	1½	70 secs.		150 days— not set
	2	24 mins.		150 days— not set
	4	75 mins. B.U.	2½ hr B.U.	40 days
diphenylamine	1	30 secs.		24 hrs. B.U.
	4	50 secs.	140 secs.	4 days
	3	50 secs.	180 secs.	5 days
diphenylguanidine	0.5	1 min.	8 mins.	6 days
	1.0	½ hour.	10 hrs.	59 days
carbazole	½	40 secs.		
	1	40 secs.	1 mins.	24 hrs. B.U.

EXAMPLE IX

Similar experiments were carried out using the same quantity of *p*-toluidine fluoborate as in Example VI, with secondary amines or an amide.

The results are reproduced in Table VI.

TABLE VI

Amine or Amide	Proportion of amine (% by weight of resin)	Setting time at stated temperature		
		160°C.	100°C.	Room temp.
Acetanilide	1	1 min.	20 mins.	12 days
N-ethylaniline	1½	80 secs.	93 mins.	150 days
N-ethyl p-toluidine	1½	12 mins.	150 mins.	150 days not set

The preferred combination is *p*-toluidine fluoborate and *p*-toluidine. Suitable proportions are from 0.5 to 2% by weight of *p*-toluidine fluoborate and from 1 to 4% by weight of free *p*-toluidine. β -naphthylamine and *p*-phenylene diamine, although effective as retardants, are not suitable for practical use owing to their carcinogenic and dermatitic effects.

p-Toluidine fluoborate is preferred to aniline fluoborate as the curing agent since it results in somewhat slower setting of the resin and thus enables a smaller proportion of retardant to be used. Curable compositions consisting of an epoxy resin to which the amine salt has been added may be used as a basis of one-part room-temperature stable compositions for a diversity of uses. For example, a one-part, room-temperature-stable mix in the form of a putty or mastic-type composition which can be applied by either a trowel or a mechanically or pneumatically operated caulking gun, can be made by

compounding an epoxy resin and the amine salt curing agent with suitable metal and mineral fillers, thickening agents, reactive and non-reactive diluents, flexibilisers and resinous modifiers.

5 Examples of suitable fillers are silica, e.g. as Kieselguhr, asbestos fibre, chopped glass fibre, metal powders which are not attacked by the amine salt, e.g. aluminium powder, titania, barium sulphate, carbon black, lithopone, ground and flaked glass, woodflour, mica, quartz and fluorspar. Fillers having an alkaline reaction cannot how- 5 ever be used. Suitable thickening agents include bentonite, colloidal silica, kaolinite.

10 Suitable reactive diluents include diglycidyl ethers, such as low viscosity glycerol-based resins, monoglycidyl ethers exemplified by such compounds as phenyl glycidyl ether, allyl glycidyl ether, and n-butyl glycidyl ether, and organic oxides such as styrene oxide, propylene oxide, an octylene oxide, α -pinene oxide, and epichlorhydrin and dioxides like a dicyclopentadiene dioxide and limonene dioxide. 10

15 Non-reactive diluents suitable for the purpose of this invention include oxygenated solvents such as ketones, ethers, and certain esters, halogenated hydrocarbons, aliphatic alcohols, and aromatic solvents, like toluene and the xylenes; other non-reactive diluents can, however, be employed. Flexibilisers and plasticizers like the polyamide resins, polysulphides, fatty diamines, and carboxylic and alcoholic hydroxyl group terminated polyesters may be employed. 15

20 Suitable resinous modifiers include urea-, aniline-, and melamine-formaldehyde resins, silicone resins, and resins based on isocyanates and furfural. 20

The substrate to which such a mastic composition is applied may be pre-heated sufficiently to promote the polymerisation of the epoxy resin on contact, or the material may be applied to a cold substrate followed by the application of moderate heat from 25 a convenient source. 25

By the use of a higher proportion of diluent or filler a solid stick or solder-like composition may be obtained which may be applied to a surface by the use of a gas or electric blowtorch operating at a temperature sufficient to melt the composition and give a flowable and workable material and subsequently polymerise the epoxy resin. 30

30 Single-mix compositions stable at room temperature and suitable for use as adhesives may also be prepared on the basis of any epoxy resin and the amine salt curing agent together with fillers and diluents. Articles to be joined may be coated with the composition, clamped together and heated to moderate temperatures, e.g. 100° C., to effect cure. Articles coated with such compositions may if desired be stored at ambient 35 temperatures for prolonged periods without polymerisation occurring, and subsequently joined by clamping two coated surfaces together and then heating them. Materials which may be joined include metal, glass, brick, ceramic and wood. Excellent bonds can be obtained at elevated temperatures even when these are not much greater than ambient temperature. 35

40 A single-mix composition for surface coating can be obtained by the addition of solvents to a mixture of epoxy resin and the amine salt to give a composition of a consistency suitable for application by brush, roller, dipping, flow coating or spraying. Compositions of this kind are stable at room temperature for long periods, thus giving a long and useful working life. After application the coating may be conveniently cured 45 by the application of heat from infra-red lamps, electric elements, or by gently heating with an open flame. The chemical resistance of such a surface coating, particularly to acids, alkalis, and common solvents, is excellent at ambient temperatures. 45

50 Still other compositions comprising an epoxy resin and the amine salt are suitable for potting, encapsulating, and embedding of electronic components, the production of moulding powders, the formulation of sealing, joining and caulking compounds, and the manufacture of plastic moulds. 50

WHAT WE CLAIM IS:—

1. A composition of matter which sets solid on heating and which comprises an epoxy resin having a 1,2-epoxy equivalency greater than one and a curing agent consisting of a salt formed between an amine and hydrofluoboric acid. 55
2. A composition according to claim 1 in which the epoxy resin is that made by reacting bis-(4-hydroxy-phenyl)-2,2-propane with epichlorhydrin in alkaline solution.
3. A composition according to claim 1 or claim 2 in which the amine is an aromatic amine.

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4. A composition according to claim 1 substantially as described in Example III or Example IV herein.
5. A process in which a composition according to any of the preceding claims is made up at room temperature, stored for a period of 24 hours or more without substantial polymerisation and then caused to polymerise by heating.
- 5 6. A composition of matter, which sets solid on heating and which comprises (i) an epoxy resin having a 1,2-epoxy equivalency greater than one, (ii) a curing agent consisting of an aromatic amine salt of hydrofluoboric acid and (iii) a proportion of a free primary or secondary aromatic amine or primary or secondary aromatic amide not exceeding 5% by weight of the resin.
- 10 7. A composition according to claim 6 in which the aromatic amine salt is a primary aromatic amine salt.
8. A composition according to claim 6 or claim 7 in which the free amine is *p*-toluidine.
- 15 9. A composition according to claim 6, substantially as described in any of Tables II to IV.
10. A process in which a composition according to any of claims 6 to 9 is made at room temperature, stored for a period of 24 hours or more without substantial polymerisation and then caused to polymerise by heating.

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